TO DETERMINE THE REFRACTIVITY OF GASES AVAILABLE ONLY IN MINUTE QUANTITIES.

ON a former occasion [1] I described a refractometer capable of dealing with rather small quantities (12 c.c.) of gas. The optical tubes, one of which would contain the material under investigation and the other air, were of brass, 20 cm. in length and 6 mm. in bore, and were traversed by two pencils of light from the same origin, subsequently brought to interference in the observing telescope. For this purpose the object-glass of the telescope was provided with two parallel slits opposite the axes of the tubes. The image of the original slit, formed in the focal plane, was examined through a high-power cylindrical lens, constituting the eye-piece of the telescope, and exhibited the familiar pattern of interference bands the position of which shifts with changes in the densities of the gases occupying the tubes. With this apparatus, and using pressures not exceeding one atmosphere, it was possible to compare refractivities $(\mu - 1)$ with a relative accuracy of about one-thousandth part.

In recent conversation my son, the Hon. R. J. Strutt, raised the question as to the minimum quantity of gas upon which a determination of refractivity could be made, having in mind such rare gases as the radium emanation. Towards answering it I have made a few experiments dealing merely with the optical side of the question.

A reduction of volume in the gas tube implies a reduction of length below the 20 cm. of the apparatus just referred to, and this carries with it a loss of accuracy. A reduction to 2 cm. should leave possible an accuracy of at least 1 per cent., and this was the length chosen. As the inquiry was limited to the optical conditions, it was unnecessary to close the ends, and thus the tubes reduced themselves to two parallel tunnels through a block of paraffin 2 cm. thick. They were prepared by casting wax (from a candle) round two similar sewing needles of suitable diameter previously secured in a parallel position. The rest of the apparatus was merely an ordinary spectroscope arrangement (without prism). Sunlight admitted through a slit, and rendered parallel by the collimating lens, traversed the double tunnel, and was received by the observing telescope focussed, as usual, upon the slit. It is necessary, of course, that the length of the slit be perpendicular to the plane containing the axes of the tunnels.

The appearance of the bands as seen with a given telescope depends upon the size of the apertures and upon their distance apart. The width of the bands is inversely as the distance between the centres of the apertures (tunnels), and the horizontal diameter of the luminous field upon which the bands are seen is inversely as the diameter of the apertures themselves. Since a large number of bands is not required, small and rather close apertures are indicated. The only question is as to the amount of light. If we suppose the apertures and their distance apart to be proportional, we may inquire as to the effect of linear scale L. Here a good deal may depend upon the relative values of length of slit, focal length of collimator, length as well as diameter of tunnels. In my apparatus the slit was short, and the height, as well as the width of the field of view, was determined mainly by diffraction. If we suppose the slit very short, the calculation is simplified, though this cannot be the most favourable arrangement. With a given width of slit the whole light in the field of view is then proportional to L^2. Since the angular area of the field practically

varies as L^{-2}, it would seem that the brightness varies as L^4. This would impose an early limit upon the reduction of L; but there are other factors to be regarded. In order to secure an angular field of given size, we must use an eye-piece the magnifying power of which is proportional to L. This consideration changes L^4 back to L^2. Nor is this all. With a given eye-piece the admissible width of primary slit varies inversely as L, and thus, finally, the brightness of a field of given angular width, and containing a given number of bands, varies as L simply.

In the earlier experiments the tunnels were of $\frac{3}{4}$ mm. bore, and were too widely separated. In order to see the bands well, a very powerful eye-piece was needed. An attempt to gain light by substituting a cylindrical lens (very successful in the former apparatus, where the beams are limited by *slits*) for the spherical lenses of the eye-piece showed little advantage. Subsequently smaller tunnels were prepared $\frac{1}{2}$ mm. in bore, and so close that the distance of the nearest parts was rather less than the diameter of either. These gave splendid bands with the ordinary eye-piece of the spectroscope, and I estimated that there should be no difficulty in setting a web correctly to one-twentieth of a band.

The capacity of one of these passages is about 4 cubic millimetres, and I have no doubt a further reduction might be effected, so far as the optics is concerned; but the further such reduction is carried the greater, probably, would become the difficulties of manipulation. The mere closing of the ends of such small tubes with plates of glass would not be an easy matter. In order to prevent encroachment upon the course of the light, it might be necessary to enlarge the ends so as to allow a little more room for overflow of cement. For the present I content myself with showing that it is possible to obtain well-formed black bands on a sufficient angular scale with light which has traversed tubes 2 cm. long and $\frac{1}{2}$ mm. in bore.   RAYLEIGH.

GAY-LUSSAC'S LAW—ITS CENTENARY.

GAY-LUSSAC'S law regarding the composition of gases by volume was made known about a hundred years ago. The paper in which he elaborated it, having been read to the Société philomatique on December 31, 1808, was published in the Mémoires de la Société d'Arceuil in the following year. Since then the law has come to have a history of its own. Chemists were at a loss and made many efforts to get it and the atomic theory to suit one another, and the place of the law in science, though not now likely to change, was for long unsettled and dubious.

Ostwald puts the law in the following way :—" If several gases appear or disappear in a chemical change, they do so always in simple ratios by volume." For example, one volume of hydrogen and one of chlorine yield two volumes of hydrochloric acid, and, again, one volume of oxygen and two volumes of hydrogen give two of steam.

The composition of nitrous and nitric oxides and numerous other gases was discovered for the first time by Gay-Lussac. But no one who has paid much attention to the history of science can be surprised that observations had been made earlier in the same field. William Higgins knew that hydrogen and oxygen combine, yielding water, in the proportion 2 : 1, and this was probably only a version of Cavendish's result. He knew also Austin's experiment proving that sulphuretted hydrogen contains its own volume of hydrogen, and he had himself observed that sulphur dioxide contains its own volume of oxyyen. It must

[1] Proc. Roy. Soc., vol. lxiv., p. 95, 1898 ; Scientific Papers, iv., p. 364.

be admitted that Higgins, who stated these facts and reasoned very justly upon them in his "Comparative View of the Phlogistic and Anti-phlogistic Hypotheses" (1789), did not give any sign, by collating them, that he felt himself on the threshold of a great discovery. Again, Gay-Lussac and Humboldt, taking up the study, for purposes of eudiometry, of the combination of hydrogen and oxygen, found the ratio between these gases to be 2 : 1 as nearly as they could measure. This was in 1804. The observation arrested Gay-Lussac's attention. Curious to find if other suchlike cases exist, he began work which resulted in the discovery of his law, one of the most important in science.

Gay-Lussac, like Newton, did not form hypotheses. The memoir in which he set forth his work is remarkably free from speculative matter. His conviction was that " in natural science, and above all in chemistry, generalisation should come after and not before a minute knowledge of each fact." And assuredly the history of Gay-Lussac's law in science does show that a " law of nature " may prove a dangerous weapon to the man who puts it to theoretical and practical uses, before its range and bearings in nature have been accurately fixed.

The law when published aroused the widest interest. The world of science was just then pondering the atomic theory in the form impressed on it by Dalton, and it was obvious that theory and law must stand in the most intimate relation to one another. Strangely enough, the law was objected to by Dalton of all people, and by him alone. In the second part of his " New System of Chemical Philosophy," published in 1810, he made strictures on it, and concluded :—" The truth is, I believe, that gases do not unite in equal or exact measures in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments. In no case, perhaps, is there a nearer approach to mathematical exactness, than in that of one measure of oxygen to two of hydrogen; but here the most exact experiments I have ever made gave 1·97 hydrogen to 1 oxygen." Berzelius wrote to Dalton protesting in the most courteous way against the part of the atomic theory " which obliges you to declare as inaccurate the experiments of Gay-Lussac, on the volumes in which gases combine. I should have thought rather that these experiments were the finest proof of the probability of the theory; and I confess to you, that I will not so readily think Gay-Lussac at fault, especially where the point is one of good or of bad measurement." Nothing, however, could ever remove the distrust Dalton felt in the law.

The chemists who accepted both Dalton's theory and Gay-Lussac's law had themselves to solve the problem of defining the relation between the two. No more than Dalton would Gay-Lussac do anything to help them. Even as late as the year 1814, in his memoir on iodine, and in the one on prussic acid of the following year, he ignores the atomic theory. He uses the word " molecule " for the sake of convenience, and that is all. Yet there must be a connection between the specific gravities, that is, the weights of equal volumes, of different gases and their atomic weights. This connection is the primary subject of a paper by Prout, published in 1815. Here he advanced his famous hypothesis that the atomic weights of the elements are multiples of the atomic weight of hydrogen, but there is good reason to think that the hypothesis was conceived after the data had been rounded off.

Berzelius had already, in 1813, if not earlier, given his solution of the problem. This was his " volume-theory," that equal volumes of different gases contain the same number of atoms. This hypothesis affords a basis of a purely physical kind for the determination of atomic weights, for it means that the atomic weights of different gases stand in the same ratio to one another as the weights of equal volumes of the gases.

The " volume-theory," plausible as it seems, involved its author in difficulties one after another, which finally became overwhelming. One arises as soon as the theory is formulated. Each atom of hydrogen, on combining with chlorine, could, as Berzelius and Dalton understood the atom, yield only one compound atom of hydrochloric acid. But the volume of the hydrogen is half that of the hydrochloric acid which it produces, so that the atom of the element occupies only half the volume of the compound atom. Hence the theory must either be limited to elements, or given up altogether. Years before Dalton had to face the same difficulty in the case of nitric oxide. What he did at first was to abandon outright the hypothesis that atoms of different gases have the same volume, and then to object even to Gay-Lussac's law. Dalton was " for thorough." What Berzelius did was to make the " volume-theory " apply only to the elements.

In course of time another difficulty appeared. The atoms of many important elements seemed to enter into combination only by pairs. This strange result arose in the following way. Berzelius began in the year 1826 to ascribe the general formula RO to all strong bases. Now, by the chemical equation for the formation of a chloride from a base—$RO + H_2Cl_2 = RCl_2 + H_2O$—it is plain that the amount of acid needed to form a chloride with one molecule of a base contains two atoms of hydrogen and two of chlorine. That is, as Berzelius saw, the hydrogen enters into chemical combination in pairs, and so does the chlorine atom.

This, be it noted, involves a conception of the element which is precisely the reverse of the modern one. Hydrogen is now supposed to consist of physical atoms, each of which can be halved when it enters into chemical combination. The physical atom of hydrogen is composed of two chemical ones. Berzelius had formed the conception of a chemical atom composed of two physical ones. It applied to quite a large number of elements in addition to hydrogen, namely, to chlorine, fluorine, bromine, iodine, nitrogen, phosphorus, antimony, and arsenic.

The very natural comment on this was made by Gmelin, that the " existence of the physical atom was improbable and its adoption superfluous and troublesome." One could arrive at Gmelin's system of chemical formulæ by suppressing every pair of physical atoms in Berzelius's formulæ, and putting in a chemical atom instead. Thus H_2O became HO. Nobody could help seeing that Berzelius's system simply led the way to Gmelin's. This was a great blow to the " volume-theory," for Gmelin's system differs from Berzelius's only by leaving out the " volume-theory " and all its consequences.

The above as an objection to the theory was perceived and felt to be overwhelming only in course of time. As already explained, from the first the theory could include in its scope only the elements. But before long Berzelius had to limit the theory still further. So long as it is applied to elements the molecules of which are of the same degree of complexity, hydrogen and oxygen, for instance, the physical method of finding atomic weights is in agreement with the chemical. The ratio H_2/O_2, which the former method gives, is the same as the ratio H/O given by the latter. But this is a matter of accident. About the year 1826 Dumas succeeded in finding the vapour-density of elements such as mercury and phos-

phorus, and was therefore enabled to calculate their respective atomic weights by the physical method. For mercury the ratios are Hg/O_2 (physical) and Hg/O (chemical), and for phosphorus P_4/O_2 (physical) and P/O (chemical).

These discrepancies forced Berzelius to limit the "volume-theory" to gaseous elements, and to such as are easily converted into gas. Finally, when discrepancies, no less serious, arose in the case of sulphur and of arsenic, he decided to abandon the theory. This was in 1833, after he had held to it for twenty years.

The only sound application of the law to theoretical chemistry was made by Avogadro in 1811. In considering his teaching, it is best to set aside the word atom and its associations, at least in the first place, and to use the word "molecule" instead. Avogadro's hypothesis is that equal volumes of different gases contain the same number of molecules. In that case the weights of equal volumes of gases are proportional to their molecular weights.

The hypothesis has a special and important consequence regarding the constitution of the molecule. For instance, each molecule of hydrogen, with the necessary chlorine, yields two molecules of hydrochloric acid. But each molecule of the acid contains hydrogen, and therefore the hydrogen molecule has certainly been halved. This conception of the molecule of an element as a thing which may consist of parts is an inevitable consequence of Avogadro's hypothesis, and it was boldly accepted by him. The mere possibility of such a thing was scouted by Thomson, and Berzelius, and Graham as utterly subversive of the atomic theory. Yet it forced itself forward again and again upon Ampère, Dumas, Prout, Waterston, Krönig, Gerhardt, Laurent, Clausius. Finally, in 1860, Cannizzaro was able to convert chemists to Avogadro's hypothesis and all its consequences. Since then the hypothesis, based as it is upon Gay-Lussac's law, has been the fundamental doctrine of chemistry.

One thing about the definition of the law is worth noting. Nothing is said in it, but much is implied, regarding the conditions under which the gases are measured. The teacher would do well to direct attention to this. There is the obvious assumption that the different gases concerned in a particular experiment are measured under the same temperature and pressure. But the definition implies another assumption, namely, that different gases behave in the same way under the same conditions. Otherwise the combining ratio, say, of hydrogen and chlorine, could not remain constant over a range of temperature and pressure.

Of course, we know that the combining ratio of two gases does not remain strictly constant when the conditions alter. The fact that a gas such as carbon dioxide deviates considerably from Boyle's law and Charles's law leads to the expectation that Gay-Lussac's law is itself only an imperfect description of the facts. The expectation is verified, for even the combining ratio of hydrogen and oxygen is not strictly 2 : 1, but has been ascertained to be 2·00285 (Scott), 2·0037 (Leduc), and 2·0027 (Morley). This is an important consideration, for molecular and atomic weight data obtained on the assumption that Gay-Lussac's law is strictly accurate must be defective. The physical method cannot lead to the same result as the chemical until a correction is introduced, and then the discrepancy is found to disappear. One systematic way of making this correction has been devised and used by M. Daniel Berthelot, and another by M. Guye.

Berzelius was led into a grave numerical error by his unqualified acceptance of Gay-Lussac's law. In the year ·1819, in conjunction with Dulong, he determined the atomic weight of carbon by the physical method. The process adopted was to weigh a certain bulk of carbon dioxide and subtract the weight of the same bulk of oxygen. The difference is the weight of the carbon, on the incorrect assumption that carbon dioxide contains exactly its own bulk of oxygen. The atomic weight was found to be 76·44 ($O=100$) or 12·23 ($O=16$). This datum, which as a matter of fact is much too high, was long used in chemistry. Berzelius should not have fallen into this error, for he had received a warning two years before against the danger of the physical method. He had determined the atomic weight of sulphur by an experiment, similar to the carbon dioxide one, with sulphur dioxide, and he set aside the result, which was 103·35 ($O=100$), because it differed so much from the figure, 100·7, which he had obtained by a chemical method.

Dumas and Stas found it necessary, in the year 1839, to embark on a re-investigation of the atomic weight of carbon. Dumas had been analysing the hydrocarbon naphthalene, and had obtained the anomalous result, again and again, that the percentages of carbon and hydrogen added up to much more than 100. As a result, the atomic weight of carbon was found to be 75·00, instead of 76·44, as Berzelius had said.

This was a severe blow to Berzelius. He had endured many reverses. One cherished conviction of his had gone after another. Chlorine and nitrogen had proved to be elements and not compounds of oxygen, the "volume-theory" had become untenable, his electrochemical theory was undermined, and his system of chemistry was threatened by Gmelin. Berzelius was yet the great master of atomic-weight determination. Even that satisfaction was now denied him; none of his atomic weights was to be above suspicion any longer, all because he had made an unjustified use of Gay-Lussac's law, twenty years before. There is a strange irony in the difficulties in which Berzelius involved himself time and again by his use of this law, in view of the protest he had made against Dalton's refusal to accept it.

A. N. MELDRUM.

ANEMOGRAPHIC OBSERVATIONS IN INDIA.[1]

MOST of these memoirs are by the late Sir John Eliot, whose loss, while he was still capable of much useful work, all meteorologists deplore. They deal with the changes in wind direction and force at the stations, showing both the diurnal and the seasonal variations, and form a store-house of information for anyone who wishes to study the Indian monsoons.

Saugor Island is situated in the north-west of the Bay of Bengal on the coast, about sixty-five miles in a direct line from Calcutta, and ninety if the bends of the river are followed. The land around it is perfectly flat, and only a few feet above the sea, so that the exposure is an excellent one.

The land at Alipore is also flat, but there are many trees in the district the tops of which are level with or above the anemometer. As might be expected, the winds are far stronger at the coast station.

Saugor Island lies in the track of the circular storms (cyclones) of the Bay of Bengal, and it is of interest to compare the maximum hourly velocity in these